

EVIDENCE FROM THE ISOTOPIC COMPOSITIONS OF INDIVIDUAL MOLECULES FOR THE INDIGENEITY OF PAH IN METEORITES. M. A. Sephton¹, C. T. Pillinger¹ and I. Gilmour¹ ¹Planetary Sciences Research Institute, The Open University, Milton Keynes MK7 6AA, UK (I.Gilmour@open.ac.uk).

For the last 25 years, interest has waned for the analysis of organic compounds from many meteorites with long terrestrial histories. This was in part due to the fall of Murchison in 1969. This event provided the opportunity to analyze an uncontaminated meteorite rich in extra-terrestrial organic. Unsurprisingly, post-1969 extra-terrestrial organic research has focused on this one sample and as a result information available for comparisons between meteorites is limited..

Following our work on the Murchison^{1,2} meteorite it is now clear that the procedures developed, may allow the identification and study of extra-terrestrial compounds even in terrestrially contaminated meteorites. Supercritical fluid extraction (SFE) may allow the retention of the abundant indigenous volatile organics, demoting the terrestrial contaminants to minor components. Hydrous pyrolysis allows the production of extra-terrestrial organics from meteorites which have had their terrestrial contaminants removed by pre-extraction. Gas chromatography isotope ratio mass spectrometry (GC-IR-MS) allows the distinction between terrestrial and extraterrestrial compounds based on ¹³C composition or association with obvious synthetic trends.

Table 1: Meteorite samples

Sample	Class	Weight
Orgueil	CI1	1.51g
Cold Bokkeveld	CM2	1.90g
Renazzo	CR2	
El Djouf	CR2	1.09g
Ornans	CO3	1.89g
Colony	CO3	1.01g
Vigarano	CV3	1.80g
Allende	CV3	2.17g
Bishunpur	LL3.1	1.72g
Roosevelt County 075	H3	1.03g

Free Aromatic Compounds

Only Cold Bokkeveld, Ornans and Vigarano contained free aromatics in amounts amenable to measurement.

Cold Bokkeveld. Cold Bokkeveld contained the greatest number of free aromatic components allowing the first isotopic measurements at the molecular level for this meteorite. Toluene, phenanthrene and phenanthrene carboxylic acid were measured. Toluene (-24.1‰) represented the heaviest measurement for free toluene for any of the meteorites analyzed. Phenanthrene (-26.9‰±1.3) is isotopically heavier than its carboxylic acid derivative (-29.8‰).

Vigarano. Vigarano had only naphthalene in measurable amounts and was similar in isotopic composition to naphthalene in Ornans (-27.0±1.9).

Ornans. Ornans has a simple aromatic distribution with toluene (-29.7) and naphthalene (-30.7‰±2.1) occupying a narrow isotopic range.

All of the aromatic compounds measured from Cold Bokkeveld were not significantly enriched in comparison to terrestrial compounds, but are similar to those values obtained for similar compounds from Murchison¹.

Interestingly, phenanthrene (-26.9‰±1.3) is isotopically heavier than its carboxylic acid derivative (-29.8‰), which is the reverse of what is expected for terrestrial compounds as isotopically heavier atmospheric CO₂ is added to lighter biological hydrocarbons resulting in a net gain in ¹³C for the molecule. This argues against a terrestrial source for these compounds and suggests that they are indigenous to the meteorite. Yuen *et al.*³ suggested the synthesis of carboxylic acids from CO₂ and hydrocarbons for the compounds observed in the Murchison meteorite. This seems unlikely in the case of Cold Bokkeveld if it is assumed that the isotopic compositions of CO₂ for Cold Bokkeveld was similar to that from Murchison (+29.1‰±0.2³). This value is noticeably heavy and would have led to an overall ¹³C enrichment for the molecule. This is the reverse of what is seen between phenanthrene and its carboxylic acid derivative in Cold Bokkeveld. However, it is possible this carboxylic acid may represent the partial oxidation of a methyl phenanthrene structure. As compounds containing more ¹²C would be expected to react first to a change in a chemical environment, the lighter isotopic composition of the carboxylic acid when compared to phenanthrene would be consistent with such a scenario. In addition the methyl phenanthrene starting material would be expected to have a lighter isotopic composition than its polynuclear homologue based on measurements made on similar free compounds and macromolecular fragments of other meteorites in this study.

Ornans The measurements of free toluene and naphthalene in Ornans are unusual due to their narrow isotopic range (1‰). Isotopic differences between toluene and naphthalene both free in Murchison (16.2‰¹) and from macromolecule fragments in Murchison and other type I and II meteorites (mean = 14.9‰⁴) show a large isotopic difference between these two compounds. This may suggest that the source of free aromatics for the Ornans meteorite is isotopically homogeneous

Vigarano The aromatic content of the Vigarano SFE extract contained only naphthalene in measurable amounts. this compounds was similar in isotopic composition to naphthalene in Ornans.

Aromatics released by hydrous pyrolysis

Due to the amount of material released on pyrolysis it is unlikely that it represents embedded terrestrial contamination. These analyses therefore probably represent the first unequivocal measurements of indigenous organic components from these meteorites.

Orgueil The aromatic components in the Orgueil hydrous pyrolysate occupy a range of $-2.9 (\pm 0.8)$ to $-25.5 (\pm 1.1)$. Toluene represents the isotopically lightest compounds and propyl benzene the heaviest. Most of the major pyrolysis fragments were amenable to measurement by GC-IR-MS.

Cold Bokkeveld The macromolecule fragments produced by hydrous pyrolysis from Cold Bokkeveld have a range between $4.0\text{‰} (\pm 3.8)$ and $-22.9\text{‰} (\pm 2.3)$. Toluene represents the lightest compound measured and ethyl benzene the heaviest. Most of the major pyrolysis fragments were amenable to measurement by GC-IR-MS.

Vigarano The aromatic compounds in the Vigarano hydrous pyrolysate have isotopic compositions which range from -23.6 to $-39.4 (\pm 5.9)$. Toluene is the lightest compound in the pyrolysate and ethyl benzene is the heaviest.

Ornans The range of values for the Ornans hydrous pyrolysate extend from -24.8 to -38.9‰ . The lightest compounds were methyl phenols and the heaviest were C_4 naphthalenes.

Bishunpur Bishunpur contained only two aromatic components in the pyrolysate, toluene and dimethyl ethyl naphthalene. These compounds were almost identical in isotopic compositions (toluene -32.5‰ ; dimethyl ethyl naphthalene $-32\text{‰} \pm 2.2$).

The random smashing of a homogeneous macromolecule would produce a number of structures with similar isotopic compositions. However hydrous pyrolysis produces a number of structures with different isotopic compositions which apparently have a relationship to the number of carbon atoms in the structure. This is consistent with the macromolecule containing structures which have a "memory" of their pre-incorporation/polymerization history or some post-incorporation ordering event. As many structures are present in their high temperature isomeric forms it is likely that they are "remembering" a pre-incorporation history rather than reflecting a low temperature aqueous alteration/ordering parent body event.

Overall isotopic composition appears to differ between meteorites. Therefore different meteorites produce compounds which appear to have sampled different carbon sources. These different carbon sources may have been produced by a mass fractionation process during the formation of the meteorite parent body. As the parent body degassed carbon dioxide, which had not been converted to non-volatile organic material, would be lost leading to an enrichment in ^{13}C in the residue left behind. Varying degrees of degassing would lead to a number of carbon sources with different ^{13}C compositions. The amount of degassing which occurs is presumably controlled by temperature and therefore will be indirectly controlled by

the heliocentric distance of the parent body, size of parent body, position within parent body, etc.

References

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